THE EFFECT OF COMPETITION BY CHLORIDE AND SULFATE ANIONS ON THE ADSORPTION OF ARSENATE ION ONTO ACTIVATED ALUMINA

A Thesis

by

PATRICK JOHN JANIŠ

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2000

Major Subject: Industrial Hygiene

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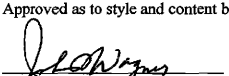
Approved as to style and content by:



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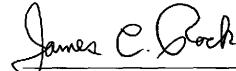

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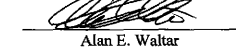

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ABSTRACT

The Effect of Competition by Chloride and Sulfate Anions on the Adsorption of Arsenate Ion onto Activated Alumina. (May 2000)

Patrick John Janiš, B.A., Texas A&M University

Chair of Advisory Committee: Dr. John P. Wagner

Interactions of arsenate ions with sulfate and chloride anions in aqueous solutions containing various amounts of activated alumina were studied in the laboratory on a batch mode basis with the goal of understanding the competition of the anions for adsorption sites on the activated alumina.

The results of this study showed that the presence of 15 meq/L chloride anion depresses the ability of the arsenate to be adsorbed by F-1 activated alumina initial liquid phase arsenate ion concentration of 5 mg/L at pH 6. Alternatively, 30 meq/L sulfate anion caused an increase in the arsenate ion adsorption. Additionally, the arsenate ion loading capacity of the activated alumina was lower with the presence of 15 meq/L chloride anion than with the presence of 30 meq/L sulfate anion. In tests with no added anions, arsenate ion loading capacity was only slightly lower than tests with 30 meq/L sulfate anion.

It is also clearly shown that the ability of activated alumina to adsorb arsenate ion is affected by the presence of chloride and sulfate anions, but the effects are not noticeable when the initial arsenate concentration to activated alumina ratio is less than 25 mg arsenate anion to 1 g activated alumina. The overall results of this study appear

applicable to improving our understanding of the performance behavior of pilot scale or commercial sized packed bed activated alumina reactors.

DEDICATION

This thesis is dedicated to my wife, Candace, and my two children, Julia and Bryant who have provided moral support to me during the entire thesis process. Their dedication to me will always be appreciated.

ACKNOWLEDGMENTS

I would like to thank my former employer, Elf Atochem North America, Inc. who allowed me to conduct these experiments in their laboratory and who provided me with much insite into the use of activated alumina for the removal of arsenic from water. Specifically I wish to thank James Adsett, Karen Vollentine, Matthew Brown, and Kimberly Sullivan who all have provided valuable assistance in completing this project.

TABLE OF CONTENTS

Page

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

A common practice for low-level arsenic removal from water since 1972 has been fixed-bed activated alumina (AA) filtration (Lake, 1990; Kartinen and Martin, 1995). This process is low-cost since the alumina can be easily regenerated many times before it is unusable (Ghosh and Yuan, 1987). Although this process is very effective at removing arsenate ion ($As(V)^+$) from deionized water, there are several cations and anions often found in groundwater that will compete with the arsenate ion for the adsorption sites on the alumina (Lake, 1990; Kartinen and Martin, 1995; Ghosh and Yuan, 1987; Rosenblum and Clifford, 1984; Huang and Stumm, 1973; Hingston and Atkinson, 1967; Kubli, 1947; Gupta and Chen, 1978; Clifford, 1982). Since this competition can lead to early loading of the alumina, requiring more frequent regeneration cycles, a shorter usable life for the alumina results (Kartinen and Martin, 1995). The objective of this study is to determine the effect of competition by chloride and sulfate anions on the adsorption of $As(V)^+$ onto activated alumina.

This study is separated into five sections, beginning with this introductory section. The second section deals with the present status of the quality of our nation's drinking water supply. Specifically, the second section is further divided into two parts. The first part deals with the history and causes of water contamination. The second part concerns the current general methods of cleaning contaminated water.

The third section explains the current status of arsenic contamination and

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This thesis follows the style and format of *Water Environment Research.*

remediation in drinking water. This section contains four parts. The first part describes the regulatory status of arsenic and drinking water. The second part explains the different types of arsenic removal processes. The next part of this section is a summary of the shortcomings of using activated alumina for arsenate ion removal, and the last part shows the need for improvement of arsenic removal processes.

The fourth section outlines the details of the experiments that were conducted for the purpose of improving the understanding of the shortcomings of activated alumina in arsenic removal, and thereby improving the successful use of it for that purpose. There are two parts in this section. The first explains the purpose and goals of the experiment and the second describes the details of the experiment, including materials, methods, and analytical analyses.

The fifth section explains the results of the experiments and details the data collected. Here the liquid phase equilibrium arsenate ion concentration, the equilibrium solid phase arsenate ion loading capacity, and the liquid phase equilibrium chloride and sulfate concentrations are discussed.

The final section identifies the conclusions that are made from the experimental data, as well as the application of the conclusions to improve the successfulness of using activated alumina to remove arsenic from drinking water. Also, suggestions for further investigation into arsenate ion adsorption onto activated alumina are made.

2. PRESENT STATUS OF THE QUALITY OF OUR NATION'S DRINKING WATER SUPPLY

2.1 HISTORY OF WATER USE AND CONTAMINATION

In the last half of the Twentieth Century there has been an increase in the demand for high quality natural water supplies in the United States and throughout the world, due to growing population and industrialization (State of California, 1975). This has led to a new interest in reusing wastewater, either directly, or indirectly as a source of drinking water and irrigation (Mathew, 1982; Sloss, 1996). Some of the contaminants in the discharged waste water, whether discharged directly into the aquifer, or discharged to an open stream, may be removed through natural processes. Some, on the other hand may remain in the water until there is human intervention to remove it. In the 1990's water quality, and specifically, drinking water quality, began to gain more attention in the United States and abroad.

As the demand for wastewater reuse continues, the wastewater effluent, once thought of as a liability, will be considered a water resource (Dennis, 1984) if it meets standards of water quality.

If the interest in wastewater reuse continues, technology for the removal of toxic materials from water will continue to grow. These toxic materials include both organic and inorganic materials. The U.S. Environmental Protection Agency (USEPA), as well as many state and local regulatory bodies, have developed lists of contaminants that must be monitored in public drinking water supplies (Gupta and Chen, 1978; Yodnane et al.,

1992). These authorities have also developed discharge limits for certain contaminants in waste streams that flow into public waters (Gupta and Chen, 1978).

2.2 CURRENT GENERAL METHODS OF DECONTAMINATING WATER

For the removal of organic materials, the most widely used process involves a filtration system using a Granular Activated Carbon (GAC) column bed (Dennis, 1984). GAC is very effective at removing a wide variety of organic (and inorganic) (Gupta and Chen, 1978) contaminants by a process called adsorption. *Adsorption* is distinguished from *absorption.* Adsorption is the attraction of selected molecules onto the surface of the adsorbent (Freifelder, 1985), while absorption is the "soaking up" of the absorbate into the absorbent, much like a sponge soaks up water. GAC is a renewable filter material, but is very expensive and requires a large amount of energy to complete the regeneration (Dennis, 1984).

GAC is also often the choice of treatment facilities for the removal of certain inorganic contaminants (Gupta and Chen, 1978; Huang and Vane, 1989). Regeneration of GAC that is contaminated with toxic metals, though, is often very expensive and sometimes impossible due to stack discharge limits at the regeneration facility.

There are numerous methods (Dennis, 1984) for removal of metals from water, including cementing, reverse-osmosis filtration, electro-disposition, chemical precipitation, ion exchange, GAC, enhanced sand filtration, and many others. One of the most conventional methods for removal of many toxic metals is lime precipitation, if the metals can be precipitated as a hydroxide or carbonate (Kartinen and Martin, 1995; Dennis, 1984). Chemical precipitation is a useful process for removing some metals, especially when they exist at very high levels in the untreated water. This process, too, can create a waste that is difficult to stabilize and expensive to manage.

3. CURRENT STATUS OF ARSENIC CONTAMINATION AND REMOVAL IN DRINKING WATER

3.1 REGULATORY STATUS OF ARSENIC AND DRINKING WATER

Metal contaminants that are sometimes found in groundwater (Bouwer, 1978; U. S. Department of the Interior, 1985) and have received publicity in the last two decades are lead (Pb), cadmium (Cd), chromium (Cr), silver (Ag), copper (Cu), zinc (Zn), selenium (Se) and arsenic (As). Sometimes these contaminants occur naturally in groundwater, and sometimes they are present because of human activity. According to USEPA (Dougherty, 1997):

> Arsenic (As) is a naturally occurring element found in the human body and is present in food, water, and air. Arsenic in drinking water occurs in groundwater and surface water and is associated with certain natural geologic conditions, as well as with contamination from human activities. Arsenic ingestion is linked to skin cancer and arsenic inhalation to lung cancer. In addition, arsenic ingestion seems to be associated with cancers of the kidney, bladder, liver, lung, and other organs. Water primarily contains inorganic arsenic species ($As(V)^{+}$ and $As(III)^{+}$), which tend to be more toxic than organic forms .

Regardless of the source, the removal of arsenic and other contaminants to a safe level must occur before the water is introduced to the drinking water supply.

Although the chemical precipitation method is sometimes used, that process alone can fail to reduce the contaminant level to the USEPA's Maximum Contaminant Level (MCL) (Kartinen and Martin, 1995). The MCL for some metal contaminants are under review by the USEPA currently. There is discussion among the regulatory bodies, for example, to reduce the MCL for

arsenic from the current standard of 50 μg/L to somewhere between 2 and 20 μg/L (Dougherty, 1997). At levels this low, chemical precipitation cannot be relied upon. It is anticipated that the lowering of the MCL will occur by the year 2001. Following is a statement by USEPA concerning their arsenic standard (Dougherty, 1997):

> In 1976 EPA issued a National Interim Primary Drinking Water Regulation for arsenic at 50 parts per billion (ppb; μg/L). Under the 1986 amendments to Safe Drinking Water Act, Congress directed EPA to publish Maximum Contaminant Level Goals (MCGLs) and promulgate National Primary Drinking Water Regulations (NPDWRs) for 83 contaminants, including arsenic. When EPA failed to meet the statutory deadline for promulgating an arsenic regulation, a citizens' group filed suit to compel EPA to do so. EPA entered into a consent decree to issue the regulation. EPA held internal work group meetings throughout 1994, addressing risk assessment, treatment, analytical methods, arsenic occurrence, exposure, costs, implementation issues, and regulatory options before deciding in early 1995 to defer the regulation in order to better characterize health effects.
>
> On August 6, 1996, Congress amended the SDWA, adding section 1412(b)(12)(A) which requires, in part, that EPA propose a NPDWR for arsenic by January 1, 2000 and issue a final regulation by January 1, 2001. The current maximum contaminant level (MCL) of 50 μg/L remains in effect until the effective date of the revised rule.

3.2 METHODS OF ARSENIC REMOVAL FROM DRINKING WATER

The chemical precipitation method of metals removal mentioned previously can be very successful with initially low levels of contaminant, but at higher initial contaminant concentrations and with the possibility of the proposed new arsenic standard levels, it is not effective alone. Although GAC has been shown to be effective at reducing the levels of inorganic arsenic to current acceptable levels (Gupta and Chen, 1978), as mentioned earlier, regeneration is difficult and disposal of the spent carbon is

expensive. Since the early 1970's, technology has been developed to remove arsenic using activated alumina (AA) (Lake, 1990; Kartinen and Martin, 1995). Other heavy metals which have been shown to be removed by AA (or GAC) are copper, manganese, lead, cadmium, chromium, selenium and silver (Dennis, 1984).

A typical AA filter system (Aluminum Company of America, 1993) consists of a column with a bed depth of 5 to 7 feet. The preferred direction of flow is downward at 2 to 4 gallons per minute per square foot of bed cross sectional area. A screen at the outlet of the column is required to keep the alumina from escaping with the treated water. Sulfuric acid is used to adjust the pH of the influent water to between 5 and 6.

A great advantage of AA over GAC is its ability to be regenerated on site while the alumina is in the column. This is accomplished (Aluminum Company of America, 1993) by first expanding the bed with a brief upflow of 0.5 to 2 percent sodium hydroxide solution at a rate of 7 to 10 gallons per minute per square foot for about 20 minutes. This removes the arsenic complexes that have been formed at the adsorption sites on the activated alumina by increasing the pH and sending the alumina contaminants out of the column in the rinsate. In some applications, several million gallons of arsenic-contaminated water can be treated to current drinking water standards, creating only a few thousand gallons of arsenic-contaminated waste water (which can be further separated with less efficient chemical precipitation/filter press methods).

It is believed that this caustic soda stripping also removes a monolayer of alumina. To complete the regeneration (Aluminum Company of America, 1993), a solution of 0.5 to 2 percent sulfuric acid is sent through the bed to purge the caustic and prepare the column for the next adsorption.

3.3 PROBLEMS WITH USE OF ACTIVATED ALUMINA FOR ARSENIC REMOVAL

It has been discovered that extended time between regeneration cycles can lead to undesirable bacteriological growth, which could foul the alumina. The backflush water generated during a regeneration cycle will contain high concentrations of the substances that have been adsorbed onto the alumina. This waste must be further treated and managed.

Unlike GAC, AA has an affinity for polar organic molecules and inorganic ions. AA has been shown to adsorb cations as well as anions. This includes the anions chloride (Lake, 1990; Rosenblum and Clifford, 1984; Clifford, 1982), sulfate (Lake, 1990; Rosenblum and Clifford, 1984; Clifford, 1982), phosphate (Bouwer, 1978; Culp and Ames, 1975), silicate (Lake, 1990), fluoride (Lake, 1990), bromide (Lake, 1990), nitrate (Lake, 1990; Clifford, 1982), nitrite (Lake, 1990), carbonate (Lake, 1990; Clifford, 1982), arsenate (Lake, 1990; Kartinen and Martin, 1995; Ghosh and Yuan, 1987; Rosenblum and Clifford, 1984; Gupta and Chen, 1978; Yodnane et al., 1992), and arsenite (Lake, 1990; Kartinen and Martin, 1995; Ghosh and Yuan, 1987; Rosenblum and Clifford, 1984; Gupta and Chen, 1978; Yodnane et al., 1992). It also includes the cations (Huang and Stumm, 1973) magnesium, calcium, strontium, and barium. The life of the AA decreases with each regeneration (Kartinen and Martin, 1995; Ghosh and Yuan, 1987; Hathaway and Rubel, 1987; Bellack, 1971; Aluminum Company of America, 1993). Each time the alumina is regenerated, small particles of it are lost in the wash-out, compaction of the bed becomes more likely, large volumes of acid and caustic are expended, many hours of labor are used, and the alumina's ability to adsorb the arsenate ion is decreased to a point lower than at the previously completed regeneration

cycle. As stated earlier, most influent waters passing through AA beds contain several different anions and cations, some at very high levels. With so many different cations and anions competing for the adsorption sites on the AA, selectivity is important in order to lengthen the usable life of the alumina.

Research has shown than pH control is very important in creating conditions appropriate for maximum arsenic adsorption, which occurs at pH levels between 5 and 6 (Lake, 1990; Kartinen and Martin, 1995; Ghosh and Yuan, 1987; Rosenblum and Clifford, 1984; Gupta and Chen, 1978; Yodnane et al., 1992; Hathaway and Rubel, 1987; Bellack, 1971, Aluminum Company of America, 1993). The control of pH gives control of the valence of the arsenic as well as the surface charges on the alumina (Ghosh and Yuan, 1987; Hingston and Adkinson, 1967; Gupta and Chen, 1978; hathaway and Rubel, 1987; Aluminum Company of America, 1993). AA predominately adsorbs arsenate ions, although is does show some ability to adsorb arsenites, but not as efficiently. In influent water that has a high concentration of arsenites, oxidation prior to introduction onto the AA has been shown to improve adsorption (Aluminum Company of America, 1993). The solid phase loading capacity of AA for arsenic increases with increasing temperature and with decreasing ion strength (Lake, 1990; Kartinen and Martin, 1995; Rosenblum and Clifford, 1984).

3.4 THE NEED FOR IMPROVEMENT OF ARSENIC REMOVAL PROCESSES

The currently accepted methods of removing arsenic may fail to meet the expected new MCL (Kartinen and Martin, 1995). Research to improve the current methods has not gained much attention in recent years and must gain some attention before our water suppliers and waste treatment facilities will be forced to resort to

inefficient and expensive methods to produce water with acceptable arsenic concentrations. There are many water suppliers who currently provide drinking water that has an arsenic concentration somewhere between the current MCL and the expected proposed MCL (Hathaway and Rubel, 1987; Steward and Kessler, 1991). Longer times between regeneration cycles would be desirable if the efficiency of the alumina were not compromised. Two factors that are known to cause early saturation of the AA are high total suspended solids (TSS) (Rosenblum and Clifford, 1984; Yodnane et al., 1992), and high competing ion concentrations (Lake, 1990; Rosenblum and Clifford, 1984; Aluminum Company of America, 1993). Problems caused by high TSS can be solved with pre-filtering. Competing ion problems can also be overcome, but ion selectivity is essential, and the processes are sometimes very expensive.

4. IMPROVING THE EFFICIENCY OF ARSENIC ADSORPTION ONTO ACTIVATED ALUMINA

4.1 PURPOSE OF THE EXPERIMENT

The purpose of this research project was to investigate the competing effects of chloride and sulfate anions on the adsorption of $As(V)^+$ onto activated alumina, in order to create a more favorable environment for the adsorption to occur. This would lead to longer use of AA before AA regeneration is necessary, and thus improve the efficiency of the process and therefore reduce the operating cost.

This goal was achieved by meeting the following secondary objectives. First, a series of four-day batch equilibrium isotherm tests were conducted on activated alumina using artificial groundwater sources consisting of arsenate ion and each of the competing anions under study in deionized water. Secondly, the equilibrium solid phase loading of the AA with the equilibrium liquid phase concentration of the arsenate ion for each competing anion studied was conducted to determine the competing effects of each anion on the loading capacity of the AA. And finally, the equilibrium liquid phase chloride and sulfate anion concentrations were examined to investigate the mechanism of the competition.

4.2 PROCEDURE

4.2.1 EXPERIMENTAL MATERIALS

Activated alumina is a porous crystalline solid with a general formula of $Al_2O_3 \cdot nH_2O$, where n = 0 - 0.6. It is produced by dehydration at 300°C to 900°C of a

variety of aluminum hydrates.[13] The AA used in this experiment was the Alcoa, F-1 Activated Alumina, with the properties shown in Table 1 (Aluminum Company of America, 1992).

Table 1--Physical properties of F-1 activated alumina.

Surface area	240 m^2/gram
Equilibrium water capacity @ 60% RH	16 wt%
Total pore volume	0.4 cc/gram
Nitrogen pore volume, (<35Å)	0.2 cc/gram
Packed bulk density	1.01 gram/cc
Mesh*	8 x 14

*8 x 14 indicates that the particles were screened so that no more than 2% of the particles are larger than 8 mesh (2.38 mm diameter) and no more than 5% of the particles are smaller than 14 mesh (1.19 mm diameter).

For proper control, all the F-1 Activated Alumina used during the experiment was conditioned as one batch. The conditioning procedure was as follows:

1) Soak the activated alumina in a 1 percent solution of NaOH for 24 hours, agitating it every eight hours by revolving the container 10 times.
2) Decant the caustic solution and thoroughly rinse with 3 bed-volumes of deionized water. Soak the alumina in a 1 percent solution of H_2SO_4 for 24 hours, agitating as in step 1.
3) Decant the acid solution and thoroughly rinse with 3 bed-volumes of deionized water.
4) Repeat steps 1 and 2.

5) Exhaustively rinse the activated alumina with deionized (DI) water until the pH of the rinsate reaches 5.0 ± 0.20.
6) Dry the conditioned activated alumina in an oven at 180°C for 12 hours, or until it is dry, and store it in a dessicator until use. (This step is omitted in large scale processes.)

The $As(V)^+$ stock anion solution was prepared by using 7.5 mL of a commercially available atomic absorption grade 1000 PPM $As(V)^+$ standard solution (using a class A volumetric pipet) and diluting it up to 1 L with deionized water in a volumetric flask. This yielded a 7.5 mg/L $As(V)^+$ solution. Except for tests of adsorption from DI water, final solutions contained total target anion concentrations of either 15 meq/L chloride, 30 meq/L sulfate, or 7.5 meq/L chloride and 15 meq/L sulfate before pH adjustment. Table 2 shows the specified mixtures for the stock target anion solutions.

Table 2--Stock anion solutions.

Anion	Reagent	F.W., Amu	Mass of Reagent, g	Total Vol., L	Anion Conc., mg/L
Cl^-	NaCl	58.5328	2.6340	1.00	1595.4
SO_4^{2-}	Na_2SO_4	142.037	12.783	1.00	8645.2

4.2.2 EXPERIMENTAL METHOD

Batch tests were performed, rather than more elaborate and unnecessary column tests. Other researchers have compared batch tests using this method to column tests for activated alumina adsorption isotherms with significantly comparable results (Rosenblum and Clifford, 1984). Although our tests produced results that were not

typical of column tests, the discrepancy is explained in Section 6. The entire experiment was conducted in the water remediation laboratory of Elf Atochem North America, Inc. in Bryan, Texas. This laboratory maintains a controlled temperature of 21.7 ± 1.0°C for optimal operation of the sensitive laboratory instruments.

A 100 ml aliquot of 7.5 mg/L $As(V)^+$ stock solution was measured, using a graduated cylinder, into a 250-mL high density polyethylene (HDPE) bottle (these bottles were new, but were not acid washed). A 50 mL aliquot of the chloride stock anion solution was measured using a graduated cylinder and added to the same bottle. Fourteen of these bottles were prepared using the sulfate stock anion solution, for a total of 28 sample bottles. Fourteen additional bottles were also prepared, containing 100 mL of the stock $As(V)^+$ solution and 50 mL deionized (DI) water. And finally, another fourteen bottles were prepared, each containing 100 mL of the stock $As(V)^+$ solution, and 25 mL each of chloride stock anion solution and sulfate stock anion solution. At this point, each of the last 56 bottles contained 5 mg/L $As(V)^+$ and either 15 meq/L of chloride anion, 30 meq/L sulfate anion, or 7.5 meq/L chloride anion and 15 meq/L sulfate anion. The final solution volume of each bottle was 150 mL.

Since it has been shown by others that the optimal pH for arsenic adsorption onto AA occurs at approximately pH = 6 (Aluminum Company of America, 1993), all arsenate ion/competing anion mixtures were adjusted to pH = 6.0 ± 0.10 with a 5% sodium hydroxide solution. A Fisher Accumet 150 pH meter was used for the measurement. Previous researchers (Aluminum Company of America, 1993) have shown that F-1 activated alumina will adsorb approximately 15 mg $As(V)^+$ onto each gram of AA at 25°C. Slightly higher loading capacities have been shown at higher temperatures (Rosenblum and Clifford, 1984). During batch tests by others (Rosenblum and Clifford, 1984), no more than 5 meq/L of any anion under study was used. Our tests

At the initial liquid phase $As(V)^+$ concentration of 5.00 mg/L $As(V)^+$, 100% adsorption should have occurred with 50 mg AA. Since one expects somewhat less than 100% adsorption in the samples containing the competing anions, the amount of AA added to each bottle varied as follows: 0, 10, 20, 30, 40, 50, and 60 mg. Appendix A shows the sample schedules in Table 7 through Table 10, describing the contents of each bottle in the experiment. As is evident from the schedule, each condition was run in duplicate.

The bottles were capped and maintained at a temperature of 22 ± 1°C for four days. Every 12 hours each bottle was inverted 5 times to ensure full contact with the alumina. This shaking method varied from the previously referenced method (Rosenblum and Clifford, 1984) which used an Eberback shaker (which operates like a "see-saw", shaking the container) operating at 140 excursions per minute with 3 cm strokes for a period of 1 day to 14 days. Our method allowed a total of four days for each sample to reach equilibrium.

At the end of four days, an aliquot was collected from each bottle and then filtered using Gelman Sciences GF Acrodisk 0.45 micron glass fiber filters and preserved with nitric acid for arsenic analysis. Another portion of each sample was held for chloride and sulfate analysis. All bottles were sealed and stored in a refrigerator at 4°C pending further analysis.

4.2.3 EXPERIMENTAL ANALYSIS

The filtered portion of each equilibrium liquid phase sample was analyzed for arsenic concentration, and the results will be recorded. The arsenic analysis was done using a Varian SpectrAA 600 Graphite Furnace Atomic Absorption Spectrometer, following EPA Method 7060 (United States Environmental Protection Agency, 1986),

using a Varian SpectrAA 600 Graphite Furnace Atomic Absorption Spectrometer, following EPA Method 7060 (United States Environmental Protection Agency, 1986), with appropriate blanks, quality control samples, duplicates, and spikes. Each sample was also analyzed for chloride and sulfate using a Dionex DX-100 Ion Chromatograph , and the results were recorded.

All analytical methods used followed current United States Environmental Protection Agency regulations for analysis of public drinking water supplies. These analyses are routinely made in this laboratory which participates in various state and national laboratory certification programs for water analysis.

5. RESULTS OF THE EXPERIMENT

5.1 EQUILIBRIUM LIQUID PHASE ARSENATE ION CONCENTRATION

As previously stated, the arsenate ion concentration of the equilibrium liquid phase of each sample container was measured. The results of each duplicate experiment were averaged and were within the relative standard deviation limit of 10%. The averaged and summarized data from the Varian SpectrAA 600 Graphite Furnace Atomic Absorption Spectrometer, following EPA Method 7060 (United States Environmental Protection Agency, 1986), are listed below in Table 3.

Table 3—Liquid phase equilibrium arsenate ion concentration for each batch sample containing an initial arsenate ion concentration of 5000 μg/L.

	Equilibrium arsenate ion concentration, μg/L			
AA, mg	**With no anions added**	**With 15 meq/L chloride anions added**	**With 30 meq/L sulfate anions added**	**With 7.5 meq/L chloride and 15 meq/L sulfate anions added**
0	5280	5044	5778	5205
10	154.9	402.8	81.28	105.1
20	36.31	59.73	22.39	29.51
30	7.394	8.710	10.96	10.00
40	<3.000	3.118	5.539	4.467
50	<3.000	<3.000	3.971	3.236
60	<3.000	<3.000	3.879	<3.000

Although the initial arsenate ion concentration in all the Table 3 samples was 5000 μg/L, contamination (of the sample bottles) is obvious since the samples that contained only arsenate ion and no activated alumina showed final concentrations

slightly higher than 5000 μg/L. In the worst case, the measured arsenate ion level was 778 μg/L higher than the amount actually added. This represents about a 15% error. Because of this, all the arsenate ion concentrations measured in these experiments are suspect by as much as 15%.

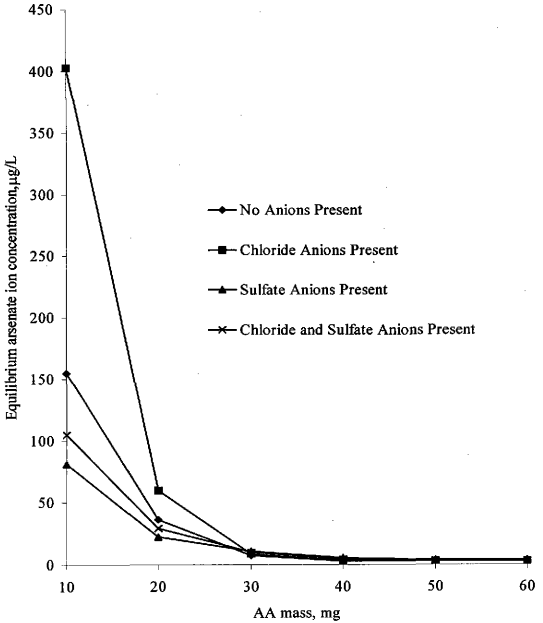

Figure 1-Liquid phase equilibrium arsenate ion concentration with varying amounts of AA in a 0.150 L solution.

Figure 1 is a graphical representation of the above data. From the first viewing of this figure, it is apparent that the interference of chloride anion, when present in the solution, suppresses the ability of the AA to adsorb the arsenate ion, especially when the ratio of AA to the initial concentration of arsenate ion is low. Sulfate, on the other hand, appears to have the reverse effect at low to medium AA to arsenate ion ratios. At the highest AA to arsenate ion ratio tested, the effects of the anions were only minimally noticeable when sulfate anion was present, and unnoticeable in all other cases.

5.2 EQUILIBRIUM SOLID PHASE ARSENATE ION LOADING

The solid phase equilibrium arsenate ion loading is a measurement of the amount of arsenate ion that is loaded (or adsorbed) onto the activated alumina per unit mass of

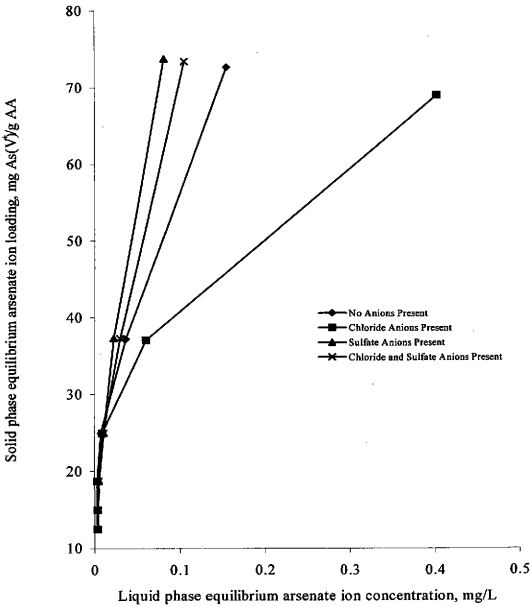

Figure 2-Solid phase equilibrium arsenate ion loading onto AA and liquid phase equilibrium arsenate ion concentration.

AA. Others have determined that the loading capacity of the AA used in this experiment is approximately 15 mg of arsenate ion per gram of alumina, or 1.5%. This was based on column tests (Rosenblum and Clifford, 1984) using beds of AA that have been conditioned in a similar way to the AA used in the present experiment. The present experiment, however, used batch tests, which, among other characteristics, allows for a much longer residence time for the arsenic-alumina interaction. Solid phase equilibrium arsenate ion loading capacities in these batch experiments ranged from 12.5 to 73.4 mg arsenate ion per gram of alumina. These ranges are on the order of 170% higher; this higher-than-expected loading capacity is discussed below in Section 6.

In order to more accurately compare the results for each trial, it is necessary to normalize the data. Figure 2, on the previous page, accomplishes this. The data used to generate the figure is listed below in Table 4. The liquid phase equilibrium arsenic

Table 4--Liquid phase equilibrium arsenate ion concentration (LPEAC) and solid phase equilibrium arsenate ion loading (SPEL) onto AA.

No anions added		Chloride anions added		Sulfate anions added		Chloride and sulfate anions added	
SPEL mg As(V)$^{+}$/ g AA	LPEAC mg As(V)$^{+}$/ L	SPEL mg As(V)$^{+}$/ g AA	LPEAC mg As(V)$^{+}$/ L	SPEL mg As(V)$^{+}$/ g AA	LPEAC mg As(V)$^{+}$/ L	SPEL mg As(V)$^{+}$/ g AA	LPEAC mg As(V)$^{+}$/ L
72.7	0.155	69.0	0.403	73.8	0.081	73.4	0.105
37.2	0.036	37.0	0.060	37.3	0.022	37.3	0.030
25.0	0.007	25.0	0.009	24.9	0.011	25.0	0.010
18.7	<0.003	18.7	0.003	18.7	0.006	18.7	0.004
15.0	<0.003	15.0	<0.003	15.0	0.004	15.0	0.003
12.5	<0.003	12.5	<0.003	12.5	0.004	12.5	<0.003

concentration was taken from Table 3; the units were converted from μg/L to mg/L by dividing by a factor of 1000. Since each sample container was sealed, the total mass of arsenate ion in each remained constant; that is to say that all the arsenate ion in the container was in one of the two phases at equilibrium. All the arsenate ion was either in the liquid phase (in the solution), or adsorbed onto the AA (the solid phase). At equilibrium, the sum of the mass of arsenate ion on the AA plus the mass of the arsenate ion in the solution is exactly equal to the initial arsenate ion mass in the solution (assuming that the empty bottles contained no arsenate ion). The initial mass of arsenate ion in each sample container was 0.750 mg. The solid phase equilibrium loading was calculated by subtracting the liquid phase equilibrium arsenate ion concentration from the liquid phase initial arsenate ion concentration (5 mg/L), then multiplying that result by the volume of the solution (0.150 L). Finally, this result is divided by the mass of AA in the sample container to give the solid phase equilibrium loading in units of mg $As(V)^{+}$/g AA.

5.3 EQUILIBRIUM LIQUID PHASE CHLORIDE AND SULFATE CONCENTRATIONS

Each sample was also analyzed at equilibrium for sulfate and chloride anion concentration using a Dionex DX-100 Ion Chromatograph. The lower limit of detection for the particular method and calibration used is 2 mg/L for chloride anion and 3 mg/L for sulfate anion. The data collected is shown in Table 5 and Table 6.

Table 5 – Equilibrium chloride anion concentrations.

	Equilibrium chloride anion concentration, mg/L			
AA, mg	No anions added	15 meq/L chloride anions added	30 meq/L sulfate anions added	7.5 meq/L chloride and 15 meq/L sulfate anions added
0	<2.000	519.8	<2.000	245.4
10	<2.000	496.9	<2.000	257.5
20	<2.000	504.3	<2.000	248.2
30	<2.000	498.9	<2.000	247.3
40	<2.000	500.2	<2.000	256.4
50	2.070	486.3	2.630	251.6
60	2.170	501.8	2.773	248.3

From Table 5 a first look at the data seems unremarkable, but when taken together with the arsenate ion concentration data, certain conclusions may be made which will be discussed in Section 6. Table 6 shows that sulfate anions formerly attracted to activated alumina is entering into the solution. This is expected since the activated alumina was conditioned using sulfuric acid which deposits sulfate anion onto the AA.

Excess sulfate anion apparently can be easily removed from the alumina under certain conditions. A least squares fit of the AA mass versus the sulfate anion concentrations in the test bottles, with no anions added, gives an excellent linear fit with r^2=0.9992. From this we conclude that in a batch test, the amount of sulfate anion that resides in the equilibrium liquid phase is directly related to the amount of AA in the container, when no additional anions are added.

Table 6 – Equilibrium sulfate anion concentrations.

	Equilibrium sulfate anion concentration, mg/L			
AA, mg	**No anions added**	**15 meq/L chloride anions added**	**30 meq/L sulfate anions added**	**7.5 meq/L chloride and 15 meq/L sulfate anions added**
0	<3.000	<3.000	3032	1344
10	184.8	196.5	3219	1678
20	345.1	317.1	3257	1740
30	506.0	454.5	3293	1751
40	688.4	582.4	3311	1707
50	826.2	739.3	3395	1693
60	998.7	921.2	3484	1744

6. ANALYSIS AND CONCLUSIONS

6.1 ACTIVATED ALUMINA ARSENATE ION LOADING CAPACITY

As mentioned previously, F-1 activated alumina has been reported to have a loading capacity of 15 mg arsenate ion per gram (Aluminum Company of America, 1993). This capacity is possible at pH 6 in a gravity flow column with an influent arsenate ion concentration of 1 PPM. At higher concentrations, the capacity is decreased, and at higher temperatures it is increased. The capacity is also dependent on total suspended solids (TSS) concentration and, of course, on the presence and quantity of other cations and anions (Aluminum Company of America, 1993).

As evidenced in Table 4, many of the loading capacities measured here were significantly higher than 15 mg/g; they ranged from 12.49 mg/g to 73.78 mg/g. This can be explained by the fact that batch tests (as performed in the present study) have somewhat different parameters than the column tests that were used to determine loading capacity. The first difference is that batch tests allow a longer residence time – four days, compared to only a few minutes, at most, in a gravity fed column. In the batch tests the arsenate ions are able to slowly make their way to the many available sites on and inside the alumina. Column tests could probably produce higher loading capacities if the flow were slowed dramatically. Secondly, in a column, certain effects like channeling can, and often do, occur which prohibits even flow throughout the bed (Aluminum Company of America, 1993). In a column scenario a large percentage of the water flowing through the column flows through a small percentage of the alumina. Techniques exist to help minimize channeling, but it still occurs, and some percentage of alumina does not make contact with the contaminated water. One of these techniques, in

a large process, involves a column with several top entrance points and several receiving points at the bottom of the column, giving the water multiple flow opportunities.

In addition to these differences, it is possible that the long contact time in a batch test can allow for migration of the arsenate ion deep into the fissures and the lattice structure of the alumina crystals. In a flowing column, an individual arsenate ion has to be quickly adsorbed by the alumina – in a long column it has lots of opportunity to be picked up, but only the "easy pick-ups" are possible, since the arsenate ion is moving and the alumina is stationary. The more difficult-to-reach sites probably require longer arsenate ion-alumina contact time due to diffusion and adsorption time. The pore size and the size of the competing anions is related to this as well. The size of the pores in the alumina varies. With longer contact times it may be possible for arsenate anions to successfully migrate into some of these pores if the sulfate anions have an affinity to be displaced by them. It may be that chloride anions, which are much smaller than sulfate anions, effectively block the exit of the sulfate anions from the pores and thereby prevent the entrance of arsenate anion.

6.2 EFFICIENCY OF ACTIVATED ALUMINA ADSORPTION OF ARSENATE ION

The anion effects that will be examined should be qualitatively the same in our present study as they would be in a similar study using a column. However, fluid mechanical factors such as channeling or deposition of fine particles in the bed interstices could severely limit bed adsorption characteristics, whereas they would have little or no influence in the present batch tests. The principle results of this study should apply to operations using activated alumina in a packed bed or a column, which is the most common set-up for arsenic removal.

As mentioned previously, research by others has shown that activated alumina is effective and efficient at removing arsenate ion from a solution. It has also been shown that certain anions, when present in the solution, inhibit the alumina from adsorbing arsenate ion efficiently. Although this present study did not attempt to quantify the effects of any particular anion on arsenate ion adsorption, several qualitative observations and conclusions nevertheless could be made.

The initial arsenate ion content per gram of AA versus arsenate removal efficiencies in Figure 3 shows that the higher the initial arsenate content per gram of AA in the influent solution, the more dramatic the effects of sulfate and chloride anion interplay appear. A high initial arsenate content per gram of AA results either when there is not enough AA in the system or when the influent arsenate ion concentration is too high. The curve for the sequence using deionized water and no additional anions shows that at maximum alumina loading (equilibrium), the alumina can remove more than 99% of the arsenate ion from a solution initially containing as much as 45 μg of arsenate ion per gram of activated alumina. However, when 15 meq/L chloride is part of the solution, the ability of arsenate ion to efficiently adsorb onto activated alumina is impaired. The greatest effect of the chloride ion on the system occurs at the higher arsenate ion to AA ratio. For example, in a solution initially containing 75.66 μg arsenate ion per gram AA, the AA was able to remove only 92% of the arsenate ion from the solution. This 7% decrease in efficiency is very significant when considering that water containing 5 PPM arsenate ion can be successfully stripped of enough arsenate ion to give an effluent that meets the current drinking water standard at 99% efficiency, but would fail to meet the standard at 92% efficiency.

Although the presence of 15 meq/L chloride anion can depress the alumina's ability to adsorb arsenate ion, the presence of 30 meq/L sulfate anion can elevate the

efficiency. As with the chloride depression, the sulfate elevation of the alumina's capacity for arsenate ion increases as the arsenate ion to alumina ratio increases.

When a mixture of 7.5 meq/L chloride anion and 15 meq/L sulfate anion is added

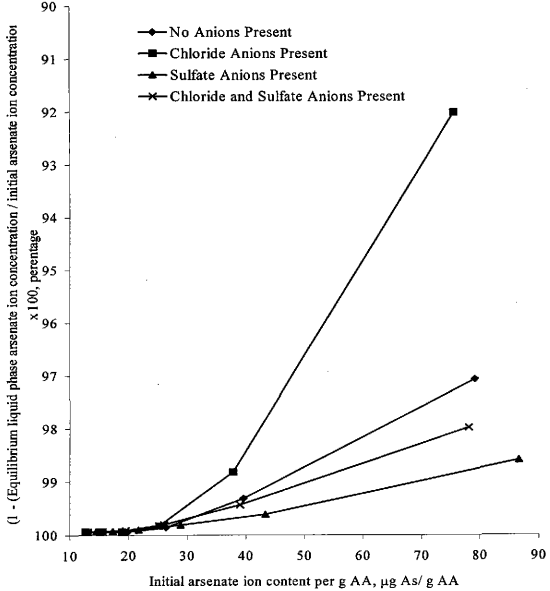

Figure 3-Initial arsenate ion content per g AA versus arsenate ion removal efficiencies.

to the deionized water, the resulting elevation of the alumina's loading capacity falls between the results of the deionized water trial and the 30 meq/L sulfate trial, as one would expect.

The net effect, in summary, is that chloride interference presents more of a problem as the initial arsenate ion concentration increases. Sulfate, either alone, or with chloride, enhances the alumina's capacity for arsenate ion as the initial arsenate ion concentration increases.

6.3 CHLORIDE AND SULFATE ANION INTERACTIONS WITH ALUMINA

It has been determined that chloride and sulfate anions play an important part in the ability of activated alumina to successfully and efficiently adsorb and retain arsenate ions. The next logical question to answer is, "Why?". In addition to the arsenic concentration analysis, the sulfate and chloride concentration analysis is also informative. The detection limit of the instrument and method used for the chloride analysis is 2 mg/L. Two lines of data, that for the trial with no anions added, and that for the trial with sulfate anions added have large parts of the curve below that threshold; not enough valid data exists to determine a trend for them, if any. The other two lines of data, that for the test which added chloride and that for the trial with both chloride and sulfate are too large. Both of these curves would appear flat and linear. For these reasons, explanations using the collected data for chloride concentration are not possible here.

The sulfate analysis is both complete and useful – it may be the key to understanding the mechanism of the adsorption. Refer first to Figure 4, which contains only two curves. There are only two curves, rather than four because, as with the chloride data, the two curves representing the two trials in which sulfate anion was added are too flat (and too large with respect to the two shown). For this reason, they are not included.

It is clear that in both cases presented, the trend is that as the initial arsenate ion content per gram of AA increases, the sulfate anion concentration in the liquid phase decreases. This is partially due to the fact that at these levels, we have less alumina in the mixture, and thus, we have less sulfate (from the initial conditioning) disassociating from it. Now as the concentration of the arsenate ion is increasing, the activated alumina

"concentration" is decreasing. Recall that in the activated alumina conditioning sulfuric acid is added, then neutralized with sodium hydroxide several times. The purpose of this is to "wash" anything adsorbed onto the alumina and replace it with sulfate anions. The sulfate anions are then replaced by arsenate ions (and certainly other ions) during the adsorption process. Because these sulfate anions are weakly "attached" to the alumina, they will release easily under proper conditions. This explains why a greater amount of

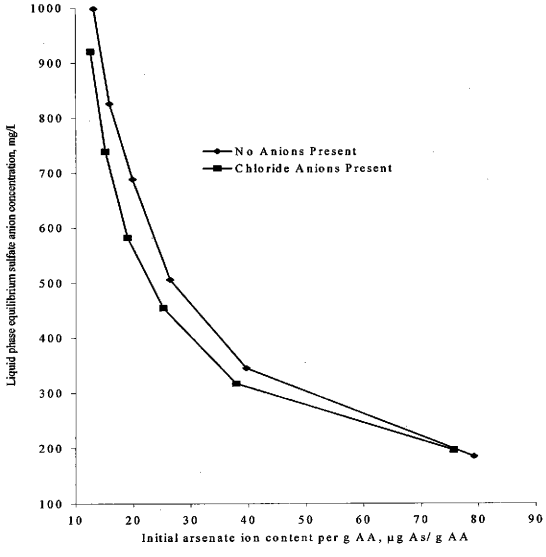

Figure 4-Equilibrium liquid phase sulfate concentrations.

alumina in the solution could produce water with higher sulfate anion concentration. Recall also our discussion of Figure 2 in Section 5.2. High solid phase loading means that the liquid phase arsenate ion is low. The more arsenate adsorbed onto the alumina, the more sulfate anions are freed from the alumina and are deposited into the liquid phase. A high concentration of sulfate ion may be of concern in some instances since the United States Environmental Protection Agency has set its maximum contaminant level at 250 mg/L. Although this level is not federally enforceable, it serves as a guideline for states public water systems (United States Environmental Protection Agency, 1999).

Figure 4 also shows that when chloride anions are added to the system, the amount of sulfate that finds its way to the liquid phase decreases. If the sulfate is not getting to the liquid phase, then it must be remaining on the alumina. The chloride anions are blocking some of the sulfate anions from releasing from the AA. This effect can partially be explained by the fact that the chloride anions, which are smaller than the sulfate anions, are blocking the AA pore exits. Sulfate anions, which are small enough to enter the AA pores during conditioning, cannot escape because the pores are "clogged up" with smaller chloride anions. This effect is more pronounced when initial concentrations of arsenate ion are low in relation to the mass of alumina. On the most fundamental level, the presence of chloride anions depressed the ability of the activated alumina to release sulfate anions and allow them to be replaced by arsenate ions. An explanation of why this is occurring may be that the chloride anions are somehow binding to the layer of sulfate anions and "locking" them into place. A more detailed identification of the location of the chloride anions could help answer this question. Future research is recommended in this area.

6.4 CONCLUSIONS

Based on the data and analysis obtained from this study, the effects of competition of chloride and sulfate on the ability of arsenate ion to be adsorbed onto activated alumina have been demonstrated. From the data it was observed that the presence of chloride anion in a solution of arsenate ion depresses the ability of the arsenate ion to be adsorbed onto activated alumina. It was further found that the presence of sulfate anion can enhance the alumina's ability to adsorb the arsenate ion. The chloride anion-induced depression of the adsorption occurs by causing the alumina not to release the sulfate anion , thus not freeing the site for the arsenate ion to adsorb. The sulfate-induced enhancement occurs when the liquid phase becomes sulfate-rich and causes the alumina to more easily release sulfate anions and thus allow for the arsenate ion to bind. Additionally, these results may help predict the effects of anions not included in this study.

Processes that are being designed to remove arsenate ion from drinking water can be better designed, from an adsorption viewpoint, with this knowledge. Arsenic-containing water that is high in chloride may need to have the chlorides removed (by chemical precipitation or by ion exchange technology) before being passed through AA - or it may be more cost effective to use a method other than activated alumina filtration (i.e. GAC, enhanced sand filtration, chemical precipitation, etc.).

This research should help further the field of knowledge in the area of arsenate ion adsorption onto activated alumina, which may lead to the development of more efficient and effective methods and processes of removing arsenic from water. It has

been shown that there are many processes that can be used, but the best process must be carefully chosen with consideration for all components of the water.

6.5 FURTHER INVESTIGATION

Continued research is necessary if we expect to continue to produce a safe drinking water supply. Further investigation into the chloride ion interaction in activated alumina adsorption of arsenate ion is recommended. This can be accomplished by carefully studying the initial and equilibrium chloride anion concentrations and by using several different initial chloride anion concentration levels.

With the very low levels of arsenate anion that are being analyzed, contamination of the samples can be an issue of concern. In future investigations using batch tests, it is recommended that pre-cleaned or acid-rinsed bottles be used to decrease the effects of sample contamination with arsenic. Apparently background airborne arsenic can cause this contamination. Failure to recognize this in the present experiments may have caused as much as 15% error.

The pH of the solution certainly has an effect on the ability of the arsenate ion to be adsorbed by the activated alumina. A future study should consider the effects of pH on the competition of arsenate, chloride, and sulfate anions for the adsorption sites on the alumina. A measurement of the equilibrium pH of the liquid phase may have been informative in the current experiments, but this information was not obtained.

REFERENCES

Aluminum Company of America (1992) F-1 Granular Activated Alumina Chemicals Product Data. Product Information Supplied by Aluminum Company of America, Industrial Chemicals Division (Vidalia, Louisiana).

Aluminum Company of America (1993) Removal of Arsenic from Water Using Activated Alumina. Product Information Supplied by Aluminum Company of America, (Vidalia, Louisiana).

Bellack, E. (1971) Arsenic Removal from Potable Water. *Journal American Water Works Association*, **63**, 454.

Bouwer, H. (1978) *Groundwater Hydrology.* McGraw-Hill Book Company, New York.

Clifford, D. (1982) Multicomponent Ion-Exchange Calculations for Selected Ion Separations. *Industrial Engineering Chemistry Fundamentals*, **21**, 141.

Culp, G. L., and Ames, C. L. (1975) Phosphorous Removal for Wastewater by Activated Alumina Columns. *Chemical Engineering Progress Symposium Series, Water 1970*, **67**, 304.

Dennis, R. L. (1984) Activated Alumina Adsorption of Trace Amounts of Chromium and Lead from Wastewaters. M.S. Thesis, Texas A&M University.

Dougherty, C. (1997) Announcement of Stakeholders Meeting on Arsenic in Drinking Water. Document 6560-50, United States Environmental Protection Agency, Office of Ground Water and Drinking Water.

Freifelder, D. (1985) *Principles of Physical Chemistry with Application to the Biological Sciences, Second Edition.* Jones and Bartlett Publishers, Inc. Portola Valley, California.

Ghosh, M. M., and Yuan, J. R. (1987) Adsorption of Inorganic Arsenic and Organoarsenicals on Hydrous Oxides. *Environmental Progress,* **6**, 150.

Gupta, S. K., and Chen, K. Y. (1978) Arsenic Removal by Adsorption. *Journal Water Pollution Control Federation,* **50**, 493.

Hathaway, S. W., and Rubel, F.(1987) Removing Arsenic from Drinking Water. *Journal American Water Works Association*, **79**, 61.

Hingston, F. J., and Atkinson, R. J. (1967) Specific Adsorption of Anions. *Nature*, **215**, 1459.

Huang, C., and Stumm, W. (1973) Specific Adsorption of Cations on Hydrous γ-Al_2O_3. *Journal of Colloid and Interface Science*, **43**, 409.

Huang, C. P. and Vane, L. M. (1989) Enhancing As(5+) Removal by a Fe(2+) - Treated Activated Carbon. *Journal Water Pollution Control Federation*, **51**, 1596.

Kartinen, E. O., and Martin, C. J. (1995) An Overview of Arsenic Removal Processes. *Desalination*, **103**, 79.

Kubli, H.. (1947) A Contribution to the Knowledge of Anion Separation by Means of Adsorption on Alumina. *Helvetica Chimica Acta*, **30**, 453.

Lake, R. L. (1990) *Point-of-Use/Entry Treatment of Drinking Water*. Noyes Data Corporation, Park Ridge, New Jersey.

Mathew, K. (1982) Groundwater Recharge with Secondary Sewage Effluent. *Technical Paper (Austrialian Water Resources Council)*, **71**, Canberra: Australian Government Publishing Service.

Rosenblum, E., and Clifford, D. (1984) The Equilibrium Arsenic Capacity of Activated Alumina. U.S. Environmental Protection Agency, EPA-600/S2-83-107.

Sloss, E.M.. (1996) *Groundwater Recharge with Reclaimed Water: an Epidemiologic Assessment in Los Angeles County, 1987-1991.* Rand, Santa Monica, California.

State of California. (1975) A "State of the Art" Review of Health Aspects of Wastewater Reclamation for Groundwater Recharge. State of California, (Sacramento, California: Department of Water Resources).

Steward, H. T., and Kessler, K. J. (1991) Evaluation of Arsenic Removal by Activated Alumina Filtration at a Small Community Public Water Supply. *Journal of the New England Water Works Association*, **105**, 179.

U. S. Department of the Interior, Bureau of Reclamation (1985) *Ground Water Manual: A Guide for the Investigation, Development, and Management of Ground-Water Resources.* (Denver: United States Government Printing Office).

United States Environmental Protection Agency (1986) Method 7060: Arsenic (Atomic Absorption, Furnace Technique). *Test Methods for Evaluating Solid Waste, Volume 1A through 1C, and Volume 2, Field Manual Physical/Chemical Methods (3rd Edition).* Rep. No. EPA/SW-846, United States Environmental Protection Agency, Washington, DC.

United States Environmental Protection Agency (1999) *Health Effects from Exposure to High Levels of Sulfate in Drinking Water Study.* Rep. No. EPA 815-R-99-001, United States Environmental Protection Agency, Washington, DC.

Yodnane, P., Patelunus, G. M., and Niece, J. E. (1992) Arsenic and Selenium Removal from Fly Ash Lechate. *Water Environment and Technology*, **4**, 31.

APPENDIX A

SCHEDULES OF SAMPLES

Table 7--Sample schedule for DI water (blank) trial.

Sample name	Volume of stock arsenate solution, mL	Volume of DI water, mL	Mass of AA, mg
As-0-1	100.0	50.00	0
As-0-2	100.0	50.00	0
As-10-1	100.0	50.00	10
As-10-2	100.0	50.00	10
As-20-1	100.0	50.00	20
As-20-2	100.0	50.00	20
As-30-1	100.0	50.00	30
As-30-2	100.0	50.00	30
As-40-1	100.0	50.00	40
As-40-2	100.0	50.00	40
As-50-1	100.0	50.00	50
As-50-2	100.0	50.00	50
As-60-1	100.0	50.00	60
As-60-2	100.0	50.00	60

Table 8—Sample schedule for chloride trial.

Sample name	Volume of Stock arsenate solution, mL	Volume of stock chloride solution, mL	Mass of AA, mg
Cl-0-1	100.0	50.00	0
Cl-0-2	100.0	50.00	0
Cl-10-1	100.0	50.00	10
Cl-10-2	100.0	50.00	10
Cl-20-1	100.0	50.00	20
Cl-20-2	100.0	50.00	20
Cl-30-1	100.0	50.00	30
Cl-30-2	100.0	50.00	30
Cl-40-1	100.0	50.00	40
Cl-40-2	100.0	50.00	40
Cl-50-1	100.0	50.00	50
Cl-50-2	100.0	50.00	50
Cl-60-1	100.0	50.00	60
Cl-60-2	100.0	50.00	60

Table 9--Sample schedule for sulfate trial.

Sample name	Volume of stock arsenate solution, mL	Volume of stock sulfate solution, mL	Mass of AA, mg
SO4-0-1	100.0	50.00	0
SO4-0-2	100.0	50.00	0
SO4-10-1	100.0	50.00	10
SO4-10-2	100.0	50.00	10
SO4-20-1	100.0	50.00	20
SO4-20-2	100.0	50.00	20
SO4-30-1	100.0	50.00	30
SO4-30-2	100.0	50.00	30
SO4-40-1	100.0	50.00	40
SO4-40-2	100.0	50.00	40
SO4-50-1	100.0	50.00	50
SO4-50-2	100.0	50.00	50
SO4-60-1	100.0	50.00	60
SO4-60-2	100.0	50.00	60

Table 10--Sample schedule for chloride/sulfate trial.

Sample name	Volume of stock arsenate solution, mL	Volume of stock chloride solution, mL	Volume of stock sulfate solution, mL	Mass of AA, mg
Cl-SO4-0-1	100.0	25.00	25.00	0
Cl-SO4-0-2	100.0	25.00	25.00	0
Cl-SO4-10-1	100.0	25.00	25.00	10
Cl-SO4-10-2	100.0	25.00	25.00	10
Cl-SO4-20-1	100.0	25.00	25.00	20
Cl-SO4-20-2	100.0	25.00	25.00	20
Cl-SO4-30-1	100.0	25.00	25.00	30
Cl-SO4-30-2	100.0	25.00	25.00	30
Cl-SO4-40-1	100.0	25.00	25.00	40
Cl-SO4-40-2	100.0	25.00	25.00	40
Cl-SO4-50-1	100.0	25.00	25.00	50
Cl-SO4-50-2	100.0	25.00	25.00	50
Cl-SO4-60-1	100.0	25.00	25.00	60
Cl-SO4-60-2	100.0	25.00	25.00	60

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